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Fluorene-Modified Zinc Porphyrin as Low-Cost Hole-Transporting Material for Efficient Perovskite Solar Cells

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Abstract The potential of porphyrin derivatives as hole-transporting materials (HTMs) for perovskite solar cells (PSCs) has been demonstrated. The structural engineering of porphyrin HTMs provides an important means for further improvement of the performance of PSCs. Herein, a zinc-porphyrin derivative (ZnP-FL) decorated with four fluorene-terminated triarylamines is presented. The lab synthesis cost of ZnP-FL is estimated to be around \$32.2/g. It exhibits good charge-transport ability and thermal stability. A high power conversion efficiency (PCE) of 19.31% is achieved by using ZnP-FL HTM ($V_{oc} = 1.08 V$; $l_{sc} = 24.08 \text{ mA} \cdot \text{cm}^{-2}$), which is distinctly higher than that of a control HTM without the fluorene groups (PCE = 17.75%; $V_{oc} = 0.97$ V; $J_{sc} = 24.04 \text{ mA} \cdot \text{cm}^{-2}$). This performance enhancement is mainly attributed to the improved open-circuit voltage, which benefits from the stabilized HOMO level of ZnP-FL. In addition, the porphyrin HTM-based PSCs show superior air and thermal stability to the device with the standard HTM spiro-OMeTAD. These results demonstrate that the low-cost and easily accessible porphyrin derivatives are promising HTMs for efficient and stable PSCs.

Key words: hole-transporting materials, porphyrin derivatives, perovskite solar cells, stability

Introduction

Perovskite (PVK) shows an attractive potential in the field of solar cells due to its extensive source of raw materials and excellent photoelectric properties. Based on the continuous optimization of PVK composition and device structure, the power conversion efficiency (PCE) of single-junction PVK



solar cells (PSCs) has reached 25.7%.¹⁻⁴ In general, the conventional architectures of PSCs are composed of electrontransporting materials, PVK layers, and hole-transporting materials (HTMs). The HTM layer plays a crucial role in achieving high performance and long-term stability of PSCs. The commonly used HTMs are limited to spiro-OMeTAD, PEDOT:PSS, and PTAA for highly efficient PSCs.^{5,6} The spiro-OMeTAD molecule suffers from complicated synthesis and purification processes, leading to a relatively high commercial price.^{7,8} The development of efficient HTMs with simple processes has become an important research direction in recent years.⁹⁻¹²

As an important molecule of natural photosynthesis, porphyrins have been widely used in catalysis,^{13,14} supramolecular assembly,^{15,16} and photovoltaics¹⁷ because of their distinctive photophysical and electronic properties and good thermal stability. In 2016, Yeh et al. first reported the use of a zinc(II) porphyrin as a HTM in PSCs to achieve a PCE of 16.6%.¹⁸ Although the potential of porphyrin-based HTMs has been demonstrated in PSCs, the PCEs have been somewhat lower than those of the current state-of-the-art HTM (spiro-OMeTAD). Only some porphyrin dimers and mixedvalency porphyrin molecules as HTMs are able to achieve the efficiency of over 19% in PSCs.^{19,20} The structural engineering of porphyrin HTMs provides an important means for further improvement of the performance of PSCs.

The synthesis processes of porphyrin derivatives are typically simple and easy to obtain in multi-kilogram scale. Their optical and electronic properties can be fine-tuned by straightforward synthetic modifications at the molecular periphery (*meso-* and β -positions) and by variation of the metal center. In this work, we present a new zinc-porphyrin HTM by introducing fluorene groups to the molecular periphery in order to improve molecule solubility and regulate the HOMO level.^{21,22} Figure 1a shows the chemical structure of the fluorene-modified porphyrin molecule which is abTHIEME

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Figure 1 (a) Chemical structure of ZnP-FL. (b) List of PCEs of > 16% achieved with porphyrin HTMs in PSCs. (c) Synthetic route to ZnP-FL and the control compound ZnP.

breviated as ZnP-FL. ZnP-FL can be readily produced by a short synthetic procedure with a low lab cost of around 32.2/g. A champion PCE of 19.31% is achieved when ZnP-FL is applied as the HTM to PSCs with the structure of ITO/SnO₂/FA_xMA_{1-x}PbI₃/HTM/Au. This performance represents one of the best efficiencies achieved by porphyrin-based small molecular HTMs (Figure 1b). Meanwhile, the device can maintain over 97% of its initial efficiency after storing in the ambient air atmosphere for 20 days. In addition, the performance of the device with ZnP-FL is distinctly superior to that with a control compound ZnP without the fluorene groups (Figure 1c). These results suggest that porphyrin derivatives are a potential alternative to spiro-OMeTAD toward the industrialization of highly efficient and stable PSCs.

Results and Discussion

The synthetic pathway toward the preparation of ZnP-FL and ZnP is shown in Figure 1c and Figure S1 in the Supporting Information. The starting material 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (1) was synthesized according to reported procedures at a laboratory cost of $1.6/g^{23}$. The C–N coupling of 1 with *N*-(4-methoxyphenyl)-9,9-dimeth-

yl-9H-fluoren-2-amine (**2**), followed by the reaction with Zn(OAc)₂ gave Zn-PL in a total yield of 66% of the two-step procedure. Full structural characterizations of ZnP-FL were undertaken using analytical and spectroscopic techniques including nuclear magnetic resonance and mass spectrometry. By using the cost model described by Dingemans, Docampo, and Osedach, the lab synthesis cost of ZnP-FL is estimated to be around \$32.2/g (Table S1), which is about a third of that of spiro-OMeTAD (\$91.67/g). Compound ZnP-FL shows good solubility in common organic solvents. In order to better understand the effect of the fluorene moieties in hole transporting, the known compound ZnP without the fluorene groups was synthesized for the purpose of comparison (Figures 1c and S2).²⁴

Density functional theory (DFT) calculations show that the HOMO of ZnP-FL is delocalized over the molecular framework (Figure 2a). Thermogravimetric analysis (TGA) shows that the decomposition temperature (T_d) for 5% weight loss is around 442.0 °C for ZnP-FL, which is slightly higher than that of spiro-OMeTAD (T_d = 430.3 °C) (Figure 2b). Besides, the differential scanning calorimetry (DSC) indicates that the glass-transition temperature (T_g) of spiro-OMeTAD is about 123.4 °C. However, no glass transition is observed for ZnP-FL and ZnP in the temperature range (50– 300 °C) measured (Figure S3). Thermal analysis suggests that ZnP-FL has comparable or slightly better thermal stability than spiro-OMeTAD.²⁵

As shown in Figure 2c, ZnP-FL exhibits a typical absorption pattern of porphyrin molecules, with a strong Soret absorption band at around 400 nm and two weak Q bands between 500 and 650 nm. The optical band gap (E_{opt}) of ZnP-FL and ZnP was calculated to be 1.95 eV from the absorption onset wavelength. As shown in Figures 2d and S4, the first anodic wave of ZnP-FL is located at +0.55 V vs. Ag/AgCl, which is slightly positive with respect to that of ZnP and spiro-OMeTAD (+0.53 V). Considering that spiro-OMeTAD has a HOMO level of -5.20 eV vs. vacuum, the HOMO levels of ZnP-FL and ZnP were estimated to be -5.22 and -5.20 eV, respectively. The deeper HOMO level of ZnP-FL is believed to be advantageous for enhancing the open circuit voltages (Voc). The HOMO levels match well the PVK HOMO level (-5.90 eV in this study), ensuring beneficial hole extraction when they are applied as the HTM (Figure 2e). According to the E_{opt} value obtained from the absorption spectra, the LUMO energy level of ZnP-FL and ZnP is estimated to be -3.27 and -3.25 eV, respectively, which can efficiently block the electron transfer from PVK to the Au electrode. The space charge limited current (SCLC) method was carried out to further quantify the hole mobility ($\mu_{\rm h}$) of these materials.²⁶ The μ_h values of the ZnP-FL, ZnP and spiro-OMeTAD were 9.94×10^{-5} , 9.00×10^{-5} measured to be and $3.75 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, respectively (Figure 2f).

Furthermore, the steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements were carried





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Figure 2 (a) Isodensity plots of the HOMO of ZnP-FL. (b) TGA analysis of ZnP-FL, ZnP and spiro-OMeTAD. (c) UV-vis absorption spectra and (d) differential pulse voltammetry of ZnP-FL, ZnP and Spiro-OMeTAD in CH₂Cl₂. (e) Energy level diagram. (f) SCLC hole mobility curves of ZnP-FL, ZnP and spiro-OMeTAD.

out to characterize the effect of ZnP-FL on hole extraction and transportation. As shown in Figure 3a, the PL intensity of the PVK film is significantly quenched after covering with a layer of ZnP-FL, suggesting the efficient hole extraction by ZnP-FL. The biexponential equation ($\tau_{ave} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$) was applied to fit the results of TPRL (Figure 3b and Table S2), where τ_1 and τ_2 represent the fast and slow decay times. The bare PVK film deposited on glass shows a long-living decay ($\tau_1 = 311.18$ ns, $\tau_2 = 746.56$ ns, $\tau_{ave} = 675.33$ ns). The average lifetime of the PVK film decreases to 392.69, 197.03 and 69.46 ns when it is covered by ZnP-FL, ZnP and spiro-OMeTAD, respectively. The de-



Figure 3 (a) Steady-state PL and (b) TRPL decay spectra of the pure PVK film and PVK film coated with ZnP-FL, ZnP and Spiro-OMeTAD.

creased transient lifetime also suggested that ZnP-FL is capable of efficient hole extraction and transport.

Figure 4 shows the atomic force microscopy (AFM) and top-view scanning electron microscopy (SEM) images of different films. The root mean square roughness of the bare PVK film is 29.372 nm, which is much higher than that of the PVK film coated with spiro-OMeTAD or ZnP-FL (9.275 and 9.858 nm, respectively). This indicates that ZnP-FL can form a complete cover layer on the surface of PVK, which is also supported by the SEM results. The smooth and uniform surface is believed to be critical for the superior photovoltaic performance of the device. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to probe the PVK film. The result of GIWAXS further indicates that the coverage of a spin-coated layer of ZnP-FL did not change the crystal structure of the PVK (Figure S5).²⁷

We fabricated typical planar n-i-p PSCs to explore the performance of ZnP-FL as a HTM. The cross-sectional view of the device is shown in Figure S6, with a structure of ITO/ $SnO_2/FA_xMA_{1-x}PbI_3/HTM/Au$. The effect of the ZnP-FL concentration on device performance is discussed firstly. As shown in Figure 5a and Table S3, with the concentration of ZnP-FL increasing from 15 to 30 mg/mL, the PCE of the device increased from 10.70% to 19.13%. As the concentration further increased to 35 mg/mL, the fill factor (FF) of the de-



Figure 4 AFM and top-view SEM images of different films, (a, d) PVK, (b, e) PVK/spiro-OMeTAD and (c, f) PVK/ZnP-FL film.



Figure 5 (a) Photocurrent density–voltage (J–V) curves of PSCs with different concentrations of ZnP-FL. (b) J–V curves of the best-performing device with different HTMs. (c) Reverse and forward J–V scans of the devices with ZnP-FL. (d) EQE spectra and integrated J_{sc} . (e) PCE efficiency statistics. (f) Stabilized PCE of devices at MPP.



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Table 1 Photovoltaic parameters of the PSC devices with differentHTMs.

Sample	J _{sc} (mA/cm ²)	$V_{\rm oc}$ (V)	FF (%)	PCE (%)	HI
ZnP-FL (R)	24.08	1.08	73.99	19.31	0.117
ZnP-FL (F)	24.10	1.07	65.84	17.05	
ZnP (R)	24.04	0.97	76.06	17.75	0.138
ZnP (F)	24.06	0.97	65.49	15.30	
Spiro-OMeTAD (R)	23.81	1.10	78.00	20.43	0.142
Spiro-OMeTAD (F)	23.77	1.06	69.29	17.53	
P-FL (R)	22.31	0.89	36.04	7.15	0.388
P-FL (F)	22.19	0.76	25.87	4.37	

vice fell sharply, leading to a significantly decreased efficiency. Therefore, the optimal concentration of ZnP-FL was determined to be 30 mg/mL. As shown in Figure 5b, a champion efficiency of ZnP-FL-based PSCs was obtained with a short-circuit current (J_{sc}) of 24.08 mA·cm⁻², a V_{oc} of 1.08 V, a FF of 73.99% and a PCE of 19.31%. This result represents one of the best efficiencies realized by a small molecular porphyrin HTM.^{18-20,24,28,29} The performance of ZnP-FL is distinctly better than that of the control compound ZnP $(J_{sc} = 24.04 \text{ mA} \cdot \text{cm}^{-2}, V_{oc} = 0.97 \text{ V}, \text{ FF} = 76.06\%, \text{ PCE} = 17.75\%)$ yet slightly inferior to that of the standard HTM spiro-OMeTAD $(J_{sc} = 23.81 \text{ mA} \cdot \text{cm}^{-2}, V_{oc} = 1.10 \text{ V}, \text{ FF} = 78.00\%,$ PCE = 20.43%) (Table 1). In addition, we also investigated the performance of the zinc-free HTM P-FL (Figure S7). The P-FL-based PSC had a PCE of 7.15%, with a V_{oc} of 0.89 V, a J_{sc} of 22.31 mA·cm⁻², and a FF of 36.04%, which indicates that the presence of Zn ions is critical to the improvement of device performance.

The hysteresis effect was evaluated according to the equation: hysteresis index (HI) = $(\eta_R - \eta_F)/\eta_R$, where η_R and $n_{\rm F}$ represent the PCE obtained in the reverse and forward scans, respectively. The device based on ZnP-FL and ZnP vielded a HI of 0.117 and 0.138, respectively, which are lower than the HI (0.142) of the spiro-OMeTAD-based device (Figure 5c and S8). Figure 5d shows the external quantum efficiency (EQE) of the devices in the range of 300–900 nm. The integrated photocurrent densities of the devices based on ZnP-FL, ZnP and spiro-OMeTAD are 22.77, 22.67 and 22.58 mA \cdot cm⁻², respectively, which are slightly inferior to the J_{sc} value obtained in the J-V measurements. The reproducibility of performance was confirmed by the efficiency statistics based on 20 devices (Figure 5e). Continuous testing at the maximum power point (MPP) for 300 s further verified the consecutive power output of the device. As shown in Figure 5f, ZnP-FL ensures a stable power output over 300 s and achieves an average efficiency of 18.42%, while spiro-OMeTAD and ZnP achieve 19.33% and 16.16%, respectively.

The long-term stability of the ZnP, ZnP-FL and spiro-OMeTAD-based devices was investigated. The PSCs were



Figure 6 (a) The PCE change of the device with different HTMs over long-term storage in air (25 °C, RH = 5%). (b) Thermal stability test at 85 °C in a N_2 atmosphere.

stored in an ambient air atmosphere with 5% relative humidity (RH) without any encapsulation. The PCE of the device with ZnP-FL barely drops in the first 5 days and it retains over 97% of the initial PCE after 20 days (Figure 6a). We also performed thermal stability tests at 85 °C on a hotplate in a glove box. After storing for 55 h at 85 °C, the devices with ZnP-FL and ZnP as HTMs show good thermal stability and maintain 73.4% and 68.7% of their initial efficiency, respectively (Figure 6b). In comparison, the efficiency of the device based on spiro-OMeTAD decreases rapidly at 85 °C and only retains 25% of the original efficiency. These results suggest that the porphyrin molecules are promising HTMs for efficient and stable PSC devices.

Conclusions

In summary, we developed a low-cost porphyrin derivative ZnP-FL with fluorene-terminated moieties and employed it as the HTM for PSCs. Because of the suitable energy level and efficient charge transporting property, a champion PCE of 19.31% ($J_{sc} = 24.08 \text{ mA} \cdot \text{cm}^{-2}$, $V_{oc} = 1.08 \text{ V}$, FF = 74.0%) is achieved with ZnP-FL. In addition, based on the good thermal stability of porphyrin molecules, the unencapsulated device with ZnP-FL maintains 97% and over 73% of their initial efficiency after aging under low humidity conditions (5% RH) for 20 days and annealing at 85 °C for 55 h, respectively. This work demonstrates that porphyrin small molecules with suitable terminal electron-donating groups are promising HTMs for efficient and stable PSCs.

Experimental Section

Materials

The chemical reagents used in the synthesis part are purchased from Innochem, J&K and Sigma-Aldrich. The materials for the fabrication of PVKs are purchased from Xi'an Polymer Light Technology in China.

Synthesis

Commercially available starting materials were purchased and used without further purification. Solvents were purified by standard methods and dried if necessary. 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (1) and *N*-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (2) were prepared according to the literature.^{22,23} The control compound ZnP is known.²⁴ NMR spectra were recorded in the designated solvent on a Bruker Avance 400 MHz spectrometer and the data are given in ppm values from the residual protons of deuterated solvents. Mass spectrometry data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer with α -cyano-4-hydroxycinnamic acid as the matrix.

Synthesis of ZnP-FL

Compound 1 (109.0 mg, 0.117 mmol), 2 (185.0 mg, 0.587 mmol), Pd₂(dba)₃ (10.74 mg, 0.012 mmol), NaO^tBu (56.36 mg, 0.586 mmol) and P(^tBu)₃ (0.58 mL, 0.247 mmol) were dissolved in toluene (20 mL) and stirred at 120 °C for 24 h under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography (eluent: petroleum ether/dichloromethane, 1/2) to yield 168.0 mg of the porphyrin product P-FL in 77% yield. ¹H NMR (400 MHz, CDCl₃): δ 9.03 (s, 8 H), 8.07 (d, J = 8.0 Hz, 8 H), 7.71 (t, J = 8.0 Hz, 8 H), 7.47-7.29 (m, 36 H), 7.02 (d, J=8.0 Hz, 8 H), 3.90 (s, 12 H), 1.53 (s, 24 H), -2.61 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 156.50, 155.25, 153.60, 148.00, 147.56, 140.91, 139.10, 135.65, 135.19, 134.09, 127.64, 127.02, 126.47, 123.04, 122.51, 120.74, 120.10, 120.00, 119.45, 118.36, 115.05, 55.58, 46.96, 31.61, 27.28, 22.67, 14.13 ppm. HRMS-MALDI-TOF: C₁₃₂H₁₀₆N₈O₄: 1866.8324. Found: 1866.8331.

A mixture of the above porphyrin product P-FL (100 mg, 0.054 mmol) and Zn(OAc)₂·2H₂O (29 mg, 0.134 mmol) was dissolved in DMF (20 mL) and stirred at 120 °C for 6 h under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 5/1) to yield 90.0 mg of ZnP-FL in 86% yield. ¹H NMR $(400 \text{ MHz}, \text{ CDCl}_3)$: δ 9.15 (s, 8 H), 8.07 (d, J = 8.0 Hz, 8 H), 7.71 (t, J=8.0 Hz, 8 H), 7.47-7.30 (m, 36 H), 7.01 (d, J=8.0 Hz, 8 H), 3.89 (s, 12 H), 1.54 (s, 24 H). ¹³C NMR (100 MHz, CDCl₃): δ 156.36, 155.22, 153.58, 150.44, 147.81, 147.67, 141.00, 139.12, 135.92, 135.46, 133.97, 131.98, 127.57, 127.03, 126.44, 122.94, 122.53, 121.11, 120.74, 120.10, 119.44, 118.26, 115.03, 55.57, 46.96, 31.64, 27.30, 22.71, 14.19 ppm. HRMS-MALDI-TOF: C₁₃₂H₁₀₄ N₈O₄Zn: 1928.7454. Found: 1928.7466.

Synthesis of ZnP

Using the same procedure for the synthesis of P-FL, the reaction of compound **1** (111.0 mg, 0.12 mmol), di-*p*-anisyl-

amine (140.4 mg, 0.61 mmol), $Pd_2(dba)_3$ (10.74 mg, 0.012 mmol), NaO^tBu (57.6 mg, 0.60 mmol) and $P(^tBu)_3$ (0.56 mL, 0.24 mmol) gave an intermediate **P** in 72% yield. This intermediate was directly used for the next transformation.

A mixture of **P** (76.1 mg, 0.05 mmol) and Zn(OAc)₂·2H₂O (32 mg, 0.15 mmol) was dissolved in DMF (10 mL) and stirred at 120°C for 6 h under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 4/1) to yield 65 mg of **ZnP** in 83% yield. ¹H NMR (400 MHz, CDCl₃): δ 9.09 (s, 8 H), 8.01 (d, *J* = 8.0 Hz, 8 H), 7.37 (d, *J* = 9.2 Hz, 16 H), 7. 31 (d, *J* = 8.4 Hz, 8 H), 6.97 (d, *J* = 8.8 Hz, 16 H), 3.85 (s, 24 H).

Device fabrication

The PSCs were fabricated according to the reported literature.³⁰ ITO (indium tin oxide) glasses were washed by sonication with ethanol, acetone, and isopropanol. Before use, ITO was cleaned with ultraviolet ozone for 20 min. Then, the ITO glass was spin-coated with SnO2 solution at 4000 rpm for 30 s and annealed at 150 °C for 30 min. After that, 691 mg PbI₂ in mixed DMF/DMSO (9/1) solution was spin-coated onto SnO₂ at 1500 rpm for 30 s, and then annealed at 70 °C for 1 min. The mixture solution of FAI/MAI/ MACl (90 mg/6.4 mg/9 mg in 1 mL of IPA) was further spincoated onto the PbI₂ layer at 2000 rpm for 30 s, followed by thermal annealing at 150°C for 15 min under ambient air conditions (30% humidity). On the top of the PVK layer was spin-coated with 35 µL of the HTM solution at 3000 rpm for 30 s. The standard Spiro-OMeTAD HTM solution was prepared by dissolving 72.5 mg of spiro-OMeTAD in a mixture of 30 µL of 4-tert-butylpyridine, 35 µL of Li-TFSI solution (260 mg of Li-TFSI in 1 mL CH₃CN) and 1 mL of chlorobenzene. The porphyrin HTM solution was prepared by dissolving 30 mg of ZnP-FL or ZnP in 1 mL of chlorobenzene in the presence of 30 µL of 4-tert-butylpyridine and 35 µL of the Li-TFSI solution in CH₃CN. Finally, 80 nm of Au layer was deposited on the hole-transport layer by thermal evaporation.

Instruments and characterization

DFT calculations are carried out using the exchange correlation functional B3LYP implemented in the Gaussian 09 package. The electronic structures of the complexes were determined using the LANL2DZ basis set for zinc, and 6–31 G* for other atoms. No symmetry constraints were used in the optimization (nosymm keyword). Solvation effects in CH_2Cl_2 were included for all calculations using the conductor-like polarizable continuum model. UV-vis absorption spectra were acquired by the UV-vis spectrophotometer (Hitachi,

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UH-4150). Differential pulse voltammetry measurements were performed on a CHI 660D potentiostat in 0.1 M n- Bu_4NClO_4 in CH_2Cl_2 by using a three-electrode system at a scan rate of 100 mV/s with an Ag/AgCl reference electrode. The working electrode was a glassy carbon electrode and a platinum coil was used as the counter electrode. The concentration of the material under study is 5×10^{-4} M. GIWAXS measurements were conducted in vacuum by Xeuss 2.0, with the incidence angle of 0.5°. Steady-state PL spectra were recorded at Nanolog FL3-2iHR with an excitation wavelength of 450 nm. TRPL spectra were performed at Delta Flex with an excitation wavelength of 450 nm. The *I–V* characteristics of the photovoltaic cells were obtained using a Keithley 2400 Source Meter under simulated one-sun AM 1.5 G illumination (100 mW·cm⁻²). The EQE was measured using an Enlitech EQE measurement system (QE-R). TGA was measured on TGA Q50 with a ramp of 10°C/min under N₂ from 40 to 800 °C. DSC was measured on DSC Q100. The working program was set from 30 to 300 °C at a scan rate of 10°C/min for three continuous cycles. The glass transition temperatures were determined during the second heating scans.

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Supporting Information

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Conflict of Interest

The authors declare no conflict of interest.

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